

Published application

Int. Cl.<sup>6</sup>: C 08 G 65/48

DE 41 03 140 A1

Reference no. P 41.03.140.7

Date of application: 2.2.91

GERMAN

Date of disclosure: 13.8.92

PATENT OFFICE

Applicant:

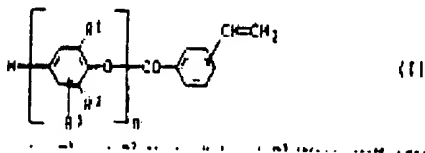
BASF AG 6700 Ludwigshefen, DE

Inventor:

Muehlbach, Klaus, Dr., 6148 Heppenheim,  
DE; Seitz Friedrich, Dr., 6701  
Friedelsheim, DE; Wicker, Michael, 3550  
Marburg, DE; Heitz, Walter, Prof. Dr.,  
3575 Kirchhain, DE

Macro-monomer(s) for prepn. Of graft copolymers – particularly  $\omega$ -(vinylbenzoyl)-  
poly-(2,6-dimethyl-1,4-phenylene] ethers

1. Macro monomers of the general formula 1,



in which,  $R^1$  and  $R^2$  means low alkyl and  $R^3$ , hydrogen or low alkyl and  $n$ , a degree of polymerisation of minimum 5.

## Description

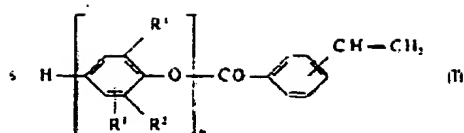
The discovery of polymers with special structures and properties is the principle task of the research. The production of copolymers by grafting through charging of macro monomers has developed as an effective method of synthesising. Macro monomers are polymers with a terminal group capable of polymerisation; they can have molecular weight of a few hundreds to several thousands.

The macro monomers can be homo-polymerised as well as copolymerised on the basis of the terminal group that can be polymerised. Grafted copolymers can be produced by copolymerisation with suitable co-monomers, whose main chain consists of the co-monomer and the terminal group of the macro monomer. The side branches are formed from the structural element of the macro monomer.

Macro monomers are described by Percec (J. Polym. Sci., Part A., Polym. Chem. 25, 2605 (1987)) on the basis of poly-(2,6-dimethyl-1,4-phenylene ether) with ether-like linked vinylbenzyl terminal group. There are well-defined macro monomers. However, it is shown that the copolymerisation of these macro monomers leads to an incomplete charge of the macro monomers under certain circumstances. It is especially observed when the molecular weight of the macro monomer is high. The incomplete feeding leads to non-uniform grafted copolymers. A later separation of the grafted copolymer and the un-converted macro monomer is not possible.

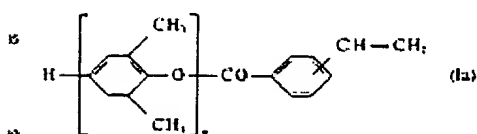
Consequently, the task consists in producing macro monomers on the basis of poly30 (2,6-dimethyl-1,4-phenylene ether), which can transform completely to the grafted copolymer through copolymerisation.

New macro monomers of the general formula 1 are the immediate subject matter of the invention,



in which,  $\text{R}^1$  and  $\text{R}^2$  means low alkyl and  $\text{R}^3$ , hydrogen or low alkyl and  $n$ , a degree of polymerisation of minimum 5.

Preferable are macro monomers of the general formula 1a,



with  $n = 5$  to 200.

Especially preferred is  $\omega$ -(4-vinyl-)benzoyl-poly-(2,6-dimethyl-1,4-phenylene ether) with a degree of polymerisation of the phenylene ether of 5 to 200.

The production of the macro monomer as per the invention takes place most easily due to the fact that one produces at first a polyphenylene ether (PPE) with suitable molecular weight of e.g. about 500 to 20000 by well-known methods and then esterifies its phenolic terminal group with the help of a vinylbenzoyl halogenide.

The required polyphenylene ether is obtained e.g. as per the information in one of the US-patent literatures 36 61 848, 32 19 625, 33 78 505, 33 06 874, 33 06 875 and 36 39 656 or as per the process starting with 2,6-dimethylphenols, which carries a halogen atom in 4-position (refer W. Risse et al, Makromol. Chem 186, 1835 (1985), or V. Percec et al, J. Poly. Sci., Polym. Lett. Ed. 24, 439 (1986).

The transformation to the macro monomers as per the invention is undertaken as usual in the presence of or with the help of an acid-binding material; especially preferable are

organic bases, which are suitable also as solvent like pyridine or bases, which are soluble on their part in a solvent for PPE (aromatic and/or halogenised non-aromatic hydrocarbon, ether) like toluene, xylene, dichloromethane, THF.

Suspendable inorganic bases or salts like (earth) alkali carbonate can also be used.

The use of the macro monomers for polymerisation follows the usual rules, e.g. for polymerisation initiated by free-radical:

For production of well-defined grafted copolymers, the macro monomer is copolymerised with suitable co-monomers. The proportion by weight of macro monomer to co-monomer can be arbitrary and, e.g., be 1 : 99 to 99 : 1, preferably from 1 : 99 to 75 : 25, and most preferably from 1 : 99 to 50 : 50.

The copolymerisation can be carried out as mass-, suspension-, emulsion- or solution-polymerisation. The mechanism of copolymerisation is itself unimportant, even though the radical polymerisation is preferred in the presence of a suitable initiator entity, if necessary.

All the monomers, which can be copolymerised with  $\omega$ -(vinylbenzoyl)-poly-(2,6-dimethyl-1,4-phenylene ether), are suitable as co-monomers. Monomers with unsaturated ethylene and/or unsaturated vinyl and/or monomers with an acrylate- and/or alkylacrylate unit can be used as monomers that can be co-polymerised.

The following can be mentioned as examples:

ethylene,  $\alpha$ -olefin, vinyl chloride, styrene, alkyl substituted styrene,  $\alpha$ -methylstyrene, vinyl- and isopropenylnaphthalene, (meth-)acrylic nitrile, (meth-)acrylic acid, maleinic acid, maleinic acid anhydride, vinyl acetate, ester of acrylic acid or meth-acrylic acid, whose alcohol part carries 1 to 20 C atoms. The co-monomers themselves can carry additional functional groups (e.g. epoxy, ester, amide etc.).

It is understood that mixtures of different co-monomers can also be used.

The polymers can be isolated by precipitation, venting the solvent in a vented extruder or a thin-film evaporator.

The grafted copolymers can be used for many purposes. Application examples are as coupling agent, compatibility agent in polymer blends or rubbers in materials.

#### **Production of poly-(2,6-dimethyl-1,4-phenylene ether)(PPE)**

Starting with p-chloro-2,6-dimethylphenol, two different products were produced as per the process described in Makromol. Chem. 186, 1838 (1985). The molecular weight was determined by means of GPC(Gel permeation chromatography).

PPE-1:  $M_n = 3,000$

PPE-2:  $M_n = 13,400$

#### **Example**

Production of  $\omega$ -(4-vinylbenzoyl)-poly-(2,6-dimethyl-1,4-phenylene ether) (VB-PPE)

VB-PPE-1 or VB-PPE-2

30 g PPE-1 and PPE-2 are dissolved under nitrogen in 350 g pyridine respectively. A 10 molar surplus of 4-vinylbenzoylchloride is added at 0° C under stirring. After 24 hours, the respective product is isolated by precipitation from methanol.

#### **Comparison test**

The terminal group that can be polymerised is introduced via an ether bond, instead of the ester bond introduced according to the invention.

25 g PPE-2 were dissolved in 250 ml toluene under nitrogen. A 10 molar surplus of 4-vinylbenzoylchloride, 10.6 g 3n NaOH and 1.08 g tetrabutylammoniumhydrogensulphate is added at room temperature as phase-transfer catalyst under stirring. After 24 hours, the product is isolated by precipitation from methanol.

The confirmatory test of total transformation took place by means of H-NMR spectroscopy, GPC and UV-spectroscopy respectively (refer Makromol. Chem. 88, 215 (1965) and J. Polym. Sc., Part A, Polym. Chem. 25, 2605 (1987)).

In all three cases, the transformation was quantitative.

Copolymerisation of the VB-PPE-2 with ethyl acrylate. 3 g VB-PPE-2 and 7 g ethyl acrylate are dissolved in 50 g toluene under nitrogen. After addition of 0.03 g AIBN as initiator entity, was polymerised for 30 hours at 60° C. The polymer formed was precipitated in a mixture of 4 parts by vol. of petroleum ether and 1 part by vol. of methanol and dried. Yield: 88 %.

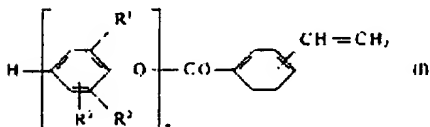
The comparison test was done as described before, but by copolymerisation of the VB-PPE with ethyl acrylate.

The yield of the comparison product was 85 %.

Both tests were examined by means of GPC and DSC. Both tests show two glass-levels in the DSC (Differential Scanning Calorimetry): -11° C and 206° C. As against this, differences are found in the GPC-diagram. While in the test according to the invention, no VB-PPE-2 more is contained in the end product, one sees in the comparison test a distinct sign of unconverted VB-PPE\*.

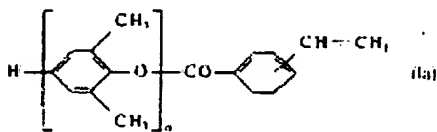
### Patent claims

1. Macro monomers of the general formula 1,



in which, R<sup>1</sup> and R<sup>2</sup> means low alkyl and R<sup>3</sup>, hydrogen or low alkyl and n, a degree of polymerisation of minimum 5.

2. Macro monomers of the general formula 1a



with  $n = 5$  to 200.

3.  $\omega$ -(4-vinyl-)benzoyl-poly-(2,6-dimethyl-1,4-phenylene ether) with a degree of polymerisation  $n$  of the phenylene ether of 5 to 200.

4. Use of the macro monomers as per claim 1 for the production of copolymers.